Chlorine Dioxide:
THE STATE OF SCIENCE, REGULATORY, ENVIRONMENTAL ISSUES, AND CASE HISTORIES

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ACUTE WATER QUALITY CRITERIA FOR CHLORITE IN FRESHWATER ECOSYSTEMS

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CHAPTER 1
INTRODUCTION AND BACKGROUND

The use of chlorine by electric utilities and other surface water users to inhibit biofouling and the chlorination of wastewater by POTWs to eliminate the discharge of pathogenic organisms are widespread practices. A number of surface water users in the Great Lakes region recently expressed an interest in using chlorine to control the zebra mussel (*Dreissena polymorpha*) which was introduced from Europe in the mid-1980s. It is well known, however, that chlorine-produced oxidants may be toxic to aquatic life when discharged into receiving waters. In addition, chlorine reacts with ammonia and chlorinated hydrocarbons to form various chloramines and trihalomethanes, which have long half-lives and similar toxicities relative to free chlorine (Fisher et al. 1999).

A number of alternatives have been proposed for chlorine. The chlorine dioxide industry has expressed an interest in the possible use of chlorine dioxide as an alternative to chlorine for control of the zebra mussel. Available literature indicates that chlorine dioxide is a powerful disinfection agent. In addition, this compound does not react with ammonia or chlorinated organics to form chloramines or trihalomethanes (Harrington et al. 1989).

Chlorine dioxide is a permanent free radical monomer which exists as a gas at room temperature. It dissolves readily in water. When chlorine dioxide is added during water treatment, it is reduced primarily to the chlorite ion (ClO_2^-) and the chloride ion (Cl^-). A small amount may also be reduced to chlorate ion (ClO_3^-). The reduction of chlorine dioxide to chlorite is rapid. Fisher and Burton (1993) found that at 25°C and in the dark, 60% of the chlorine dioxide added to a static system decayed to chlorite in 15 min and that the decay of chlorine dioxide was more rapid than that of chlorine. Reduction of chlorine dioxide to chlorite was complete in 4 h. Since chlorite is relatively stable once formed, its toxicity is important when the possible impact of chlorine dioxide usage in surface waters is considered.

Past toxicological studies conducted with chlorite have been directed towards the development of acute water quality criteria (Criterion Maximum Concentration or CMC) because short-term (4 days or less) applications one or two times a year were considered to be sufficient to control zebra mussels. The studies were conducted to provide data to meet the requirements of the

EPA acute water quality guidelines (Stephan et al. 1985). Acute toxicity studies were conducted on eight different families of freshwater aquatic organisms; three vertebrates and five invertebrates. The three vertebrates were the fish families Cyprinidae (fathead minnow, *Pimephales promelas*), Salmonidae (rainbow trout, *Oncorhynchus mykiss*), and Centrarchidae (bluegill, *Lepomis macrochirus*). The five invertebrate families were Daphnidae (*Daphnia magna* and *Ceriodaphnia dubia*), Brachionidae (rotifer, *Brachionus calyciflorus*), Hyalelladae (amphipod, *Hyalella azteca*), Hydridae (hydra, *Hydra littoralis*), and Chironomidae (midge, *Chironomus tentans)* (Fisher and Burton 1993, 1995; Burton 1995). When the data from these earlier tests were examined it was found that the sensitivity of one family (Daphnidae) was much greater than all other families tested. For example, the next most sensitive family was the Hyalelladae (amphipod) which was 44 times less sensitive. The third and fourth most sensitive families tested were the Hydridae (hydra) and the Brachionidae (rotifer) which were 98 and 1,018 times less sensitive than the Daphnidae, respectively.

EPA's water quality criteria method uses the toxicity results from the four most sensitive organisms to calculate its criteria, ignoring values from all other less sensitive organisms. An unfortunate aspect of the EPA methodology for calculating the CMC is the necessity of extrapolating to estimate the 0.05 cumulative probability for small data sets (Erickson and Stephan 1988). If extrapolations become too great, the CMC is suspect. This appears to be the case with this original chlorite data set. In addition, the disparity between the toxicity of chlorite to Daphnidae compared to all the other families tested may be forcing an unreasonably low CMC. As can be seen in Figure 1.1, chlorite is much less toxic than chlorine for all species except the daphnid when existing data are compared to the chlorine acute data used to calculate the water quality criteria (A) and when the comparison is made only on species tested with both compounds (B)(U.S. EPA 1985, Fisher and Burton 1995). Nevertheless, the chlorite CMC calculated for the original eight families with exposures up to 4 days was 0.004 mg/L as chlorite (0.009 mg/L as total residual oxidant; TRO). The CMC value for chlorite is much less than that the chlorine CMC which is 0.019 mg/L as TRO.

The water quality criteria guidelines have a number of items to be considered during the final review of the criteria (page 55 - Stephan et al. 1985). One of these is to check whether there is more than a factor of 10 difference between the four lowest mean acute values used in the calculation. For chlorite, there is a factor of 769 between the lowest and highest LC50 for these four most sensitive

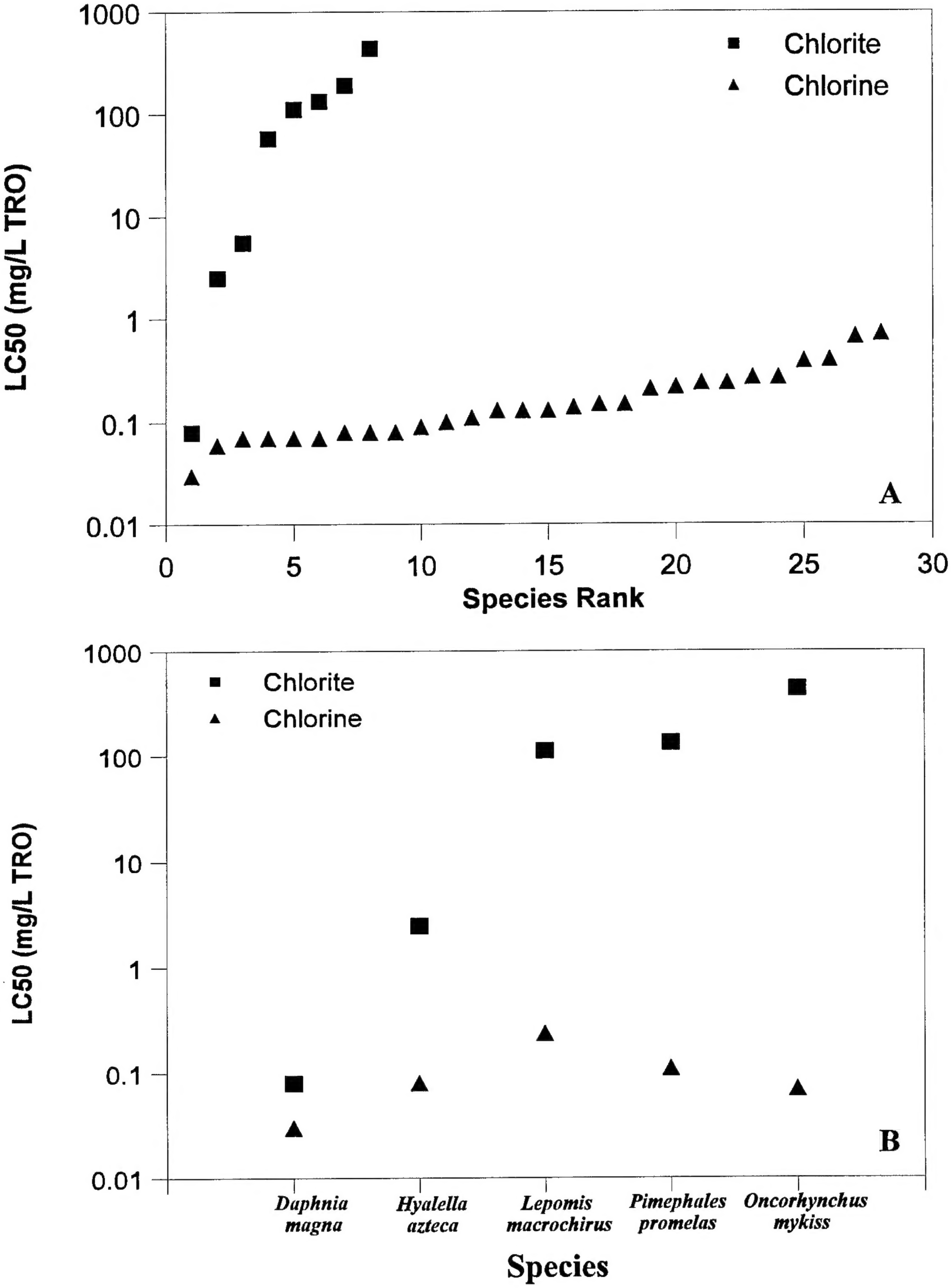

Figure 1.1 (A) LC50 species mean rank comparison between chlorine and chlorite and (B) LC50 comparisons for species tested with both chemicals

families. The guidelines then indicate that, if there is some question concerning the criteria, other criteria should be derived using appropriate modifications of the guidelines. There is little guidance on what modifications might be appropriate.

A meeting was held with EPA's Health and Ecological Criteria Division, Washington, DC, to discuss various alternative approaches to analyzing the chlorite data because of the large difference (factor of 769) between the four lowest mean acute values. Based on the acute toxicity data base for the eight families, it was agreed that an alternative approach was justified. We proposed to EPA that a probabilistic risk assessment approach be considered. In order to implement a probabilistic approach, acute toxicity data are required to describe the distribution of susceptibilities in the "universe" of species. Since the goal of EPA's water quality criteria is to protect 95% of the species/families in aquatic ecosystems, we agreed to test a sufficient number of species/families so that each represented at least 5% of the total number tested. Thus, we tested an additional 12 species/families of freshwater organisms to better define the species distribution of acute sensitivities to chlorite. Twelve additional species also provided sufficient families so that each family represented 5% of the total number of families tested. Using these additional data we examined the protection level as calculated by both the EPA water quality criteria method (CMC) and the probabilistic method (95% protection level). We also determined the 90% protection level which is frequently used in probabilistic environmental risk assessments.

CHAPTER 2
RESULTS AND DISCUSSION

The 12 additional acute toxicity tests, all of which were performed on early life stages, included two amphibians, three fish, and seven invertebrates. The amphibians tested were the frog *Rana pipiens* and the toad *Bufo americana*. The three fish were the catfish *Ictalurus punctatus*, guppy *Poecilia reticulata*, and cichlid *Cichlasoma nigrofasciatum*. The seven invertebrates were the crayfish *Procambarus clarkii*, planaria *Dugesia tigrina*, isopod *Caecidotea communis*, ostracod *Cypridopsis vidua*, copepod *Acanthocyclops robustus*, freshwater worm *Lumbriculus variegatus* and the mosquito larvae *Culex pipiens.* A detail description of the experimental protocols, measurement of chlorite concentrations in the bioassay systems, and statistical analysis of the data for the additional 12 species is given in a report to the American Chemistry Council (Fisher and Burton 2000).

The results from the current group of 12 acute bioassays are similar to the results from the earlier studies conducted with chlorite. When the data base from all of the chlorite studies (20 families) are examined, the Daphnidae family is still the most sensitive family (Table 2.1). The Daphnidae are over an order of magnitude more sensitive than the next most sensitive family the Hyalellidae and two orders of magnitude more sensitive than the most sensitive fish family tested, the Ictaluridae. It is also more sensitive than other organisms that could serve as food sources for larval fish, including the copepod (Cyclopidae) and the ostracod (Cyprididae) (Giddings, et al. 1997).

The Family Mean Acute Values (FMAVs) presented in Table 2.1 were used to calculate a Final Acute Value (FAV) and CMC by the method used in the EPA's procedure for developing water quality criteria (Stephen et al. 1985). Briefly, the FAV estimation is based on a subset of the available data near the fifth percentile. The FAV is calculated from a set of Genus Mean Acute Values (GMAV) or Family Mean Acute Values (FMAV) by (a) assigning each GMAV or FMAV a cumulative probability P_R, (b) fitting a line to ln (GMAV or FMAV) versus $\sqrt{P_R}$ using the four points with P_R nearest 0.05 and using the geometric mean functional relationship to estimate slope, and (c) calculating the FAV as the concentration corresponding to $P_R = 0.05$ on the curve. If there are less than 59 GMAVs or FMAVs, as is generally the case, the four GMAVs or FMAVs used in

Table 2.1

List of all families/species tested with LC50s (as mg/L chlorite) by sensitivity

Family	Species	LC50	SMAV[1]	FMAV[2]
Daphnidae	*Ceriodaphnia dubia* (daphnid)	0.022	0.022	0.027
	Daphnia magna (daphnid)	0.039	0.032	
		0.026		
Hyalellidae	*Hyalella azteca* (amphipod)	1.19	1.19	1.19
Astacidae	*Procambarus clarkii* (crayfish)	1.27	1.27	1.27
Planariidae	*Dugesia tigrina* (planaria)	1.34	1.34	1.34
Asellidae	*Caecidotea communis* (isopod)	1.57	1.57	1.57
Cyprididae	*Cypridopsis vidua* (ostracod)	1.63	1.63	1.63
Hydridae	*Hydra littoralis* (hydra)	2.65	2.65	2.65
Ictaluridae	*Ictalurus punctatus* (catfish)	5.79	5.79	5.79
Cyclopidae	*Acanthocyclops robustus* (copepod)	6.74	6.74	6.74
Poeciliidae	*Poecilia reticulata* (guppy)	17.45	17.45	17.45
Lumbriculidae	*Lumbriculus variegatus* (worm)	22.73	22.73	22.73
Brachionidae	*Branchionus calyciflorus* (rotifer)	27.48	27.48	27.48
Culicidae	*Culex pipiens* (mosquitoe larvae)	44.29	44.29	44.29
Centrarchidae	*Lepomis macrochirus* (bluegill)	53.14	53.14	53.14
Cyprinidae	*Pimephales promelas* (fathead minnow)	63.38	63.38	63.38
Ranidae	*Rana pipiens* (frog)	65.69	65.69	65.69
Cichlidae	*Cichlasoma nigrofasciatum* (cichlid)	86.95	86.95	86.95
Chironomidae	*Chironomus tentans* (midge)	90.67	90.67	90.67
Bufonidae	*Bufo americana* (toad)	149.60	149.60	149.60
Salmonidae	*Oncorhynchus mykiss* (rainbow trout)	208.76	208.76	208.76

[1]SMAV = Species Mean Acute Value (Geometric mean of species LC50s)

[2]FMAV = Family Mean Acute Value (Geometric mean of genera LC50s)

the calculation will always be the four lowest GMAVs or FMAVs. A computer program provided by Peter Howe of EPA, Region 5, Chicago, Ill., was used to calculate the FAV. The CMC or final protection level is calculated as one-half of the FAV.

The FAV calculated using the toxicity values in Table 2.1 is 0.049 mg/L as chlorite (0.103 mg/L as TRO). The regulatory CMC value is set at one-half the FAV or 0.025 mg/L as chlorite (0.052 mg/L as TRO). The chlorite CMC calculated for the original eight families with exposures up to 4 days was 0.004 mg/L as chlorite (0.009 mg/L as TRO). The CMC for the 20 family data base is 6.3 times greater than the CMC for the original eight families.

A very different 95% protection level is obtained if the FMAVs from Table 2.1 are used to calculate a 95% protection level using a probabilistic risk assessment approach. The method for calculating the protection level used in a probabilistic risk assessment involves plotting all species or family sensitivities on a cumulative percent rank probability scale, and calculating the concentration which will be protective of a given percent of the families tested using regression analysis (SETAC 1994, U.S. EPA 1998).

Figure 2.1 shows the LC50 distribution data for the 20 families graphed against percent rank for chlorite (as mg/L chlorite). The regression curve y intercept b[0] = -0.8914; coefficient b[1] = 0.8658; and $r^2 = 0.91$. The probit transform for the 95% protection level is 3.3551. The concentration of chlorite for a 95% protection level was calculated by the equation:

$$\text{Concentration} = 10 \text{ raised to the } ((3.3551-(b[0] + 5))/b[1] \qquad (1)$$

The 95% protection level calculated by this method is 0.135 mg/L as chlorite (0.284 mg/L as TRO). The value of 0.135 mg/L as chlorite is 5.4 times greater than the CMC calculated by the water quality criteria method. The probabilistic-derived 95% protection value of 0.135 mg/L will be recommended to EPA as the more appropriate acute water quality criterion for chlorite.

EPA uses a 95% protection level for water quality criteria; however, a less restrictive protection level (e.g., 90%) is possible if the ecological risk of chlorite discharged to surface waters is considered. We recommend that a probabilistic ecological risk assessment be considered since it is a risk assessment method which incorporates variability in toxicological effects and exposure

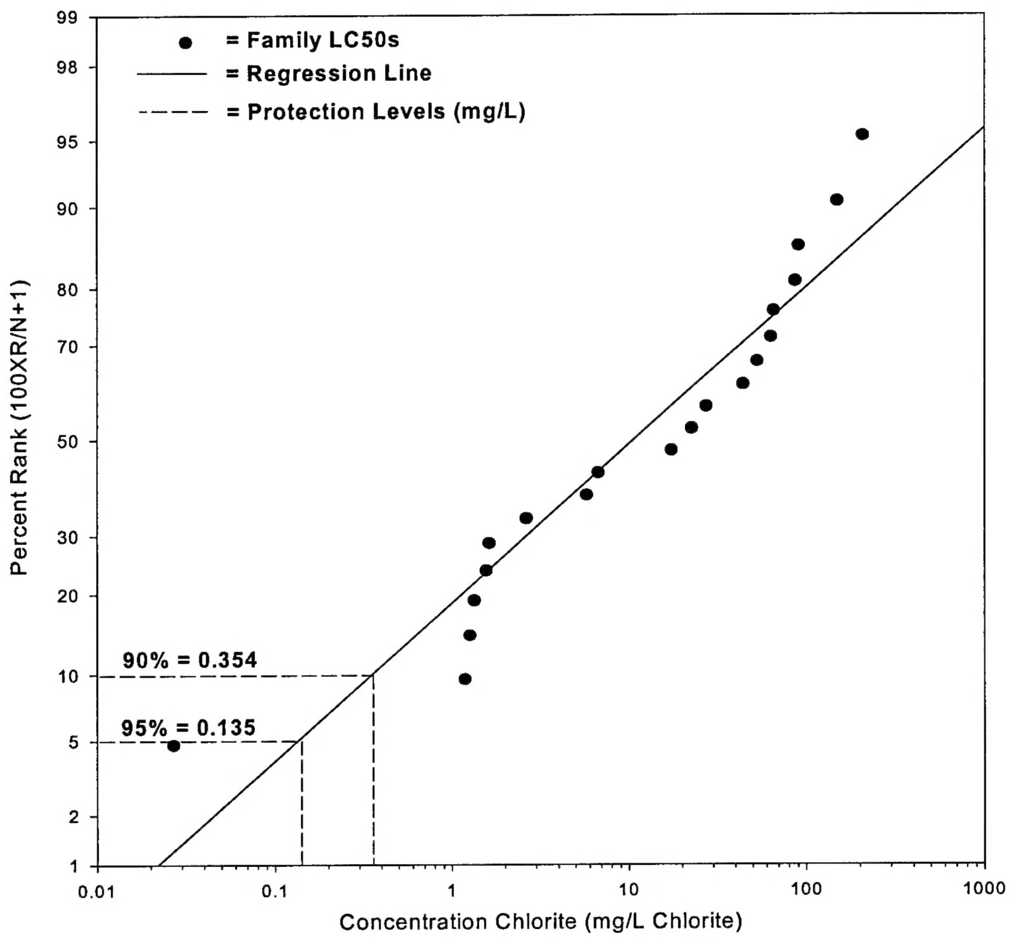

Figure 2.1. LC50 values as family percent rank for all acute toxicity tests with chlorite

concentrations in the environment. In a conventional risk assessment, the exposure concentration is expressed as a single value, the quantitative likelihood of which is unknown because it has not been placed in a probabilistic framework that captures the variability of actual environmental concentrations. Probabilistic procedures can be used for estimating exposure that take natural variation into account by providing distributions of exposure concentrations rather single exposure concentration values. Likewise, the range of susceptibility of species to substances also must be taken into account. Traditional risk assessments are based on the susceptibility of the most sensitive organism or group of organisms. As with exposure concentrations, a probabilistic risk assessment incorporates the distribution of species sensitivities. The advantage of this approach over using the most sensitive species is that it uses all relevant species toxicity data, and when compared to the exposure distributions, allows quantitative estimations of risks to aquatic organisms. Finally, the process allows consideration of usage patterns as well as the ability to incorporate all available toxicity data to assess risk.

In contrast to water quality criteria which use a 95% protection level, several groups have agreed that a 90% protection level should protect aquatic ecosystems (Health Council of the Netherlands 1993, SETAC 1994). It can be seen in Figure 2.1, that 90% of the species in the 20 family data base would be protected at chlorite concentrations up to 0.354 mg/L as chlorite (0.745 mg/L as TRO). The probit transform in equation (1) for the 90% protection level is 3.7184.

A consideration in a probabilistic ecological risk assessment is the importance of various families as food resources for fish (Giddings et al. 1997, Hall and Giddings 2000). In addition to the Daphnidae, a number of other families in the current data base can serve as food sources for fish. Thus, if one excludes the Daphnidae because of their low sensitivity relative to other invertebrates which can serve as food sources, a different set of protection levels can be calculated. The toxicity distribution data for the 20 families less the Daphnidae are shown in Figure 2.2. The regression curve y intercept b[0] = -1.2683; coefficient b[1] = 1.0879; and $r^2 = 0.93$. As was the case for the 20 family data, the probit transforms for the 90 and 95% protection levels used in equation (1) are 3.7184 and 3.3551, respectively. The 95% protection level for the 20 families less the Daphnidae is 0.451 mg/L as chlorite (0.947 mg/L as TRO). The 90% protection level for the 20 families less the Daphnidae is 0.972 mg/L as chlorite (2.042 mg/L as TRO). The 95 and 90% protection levels

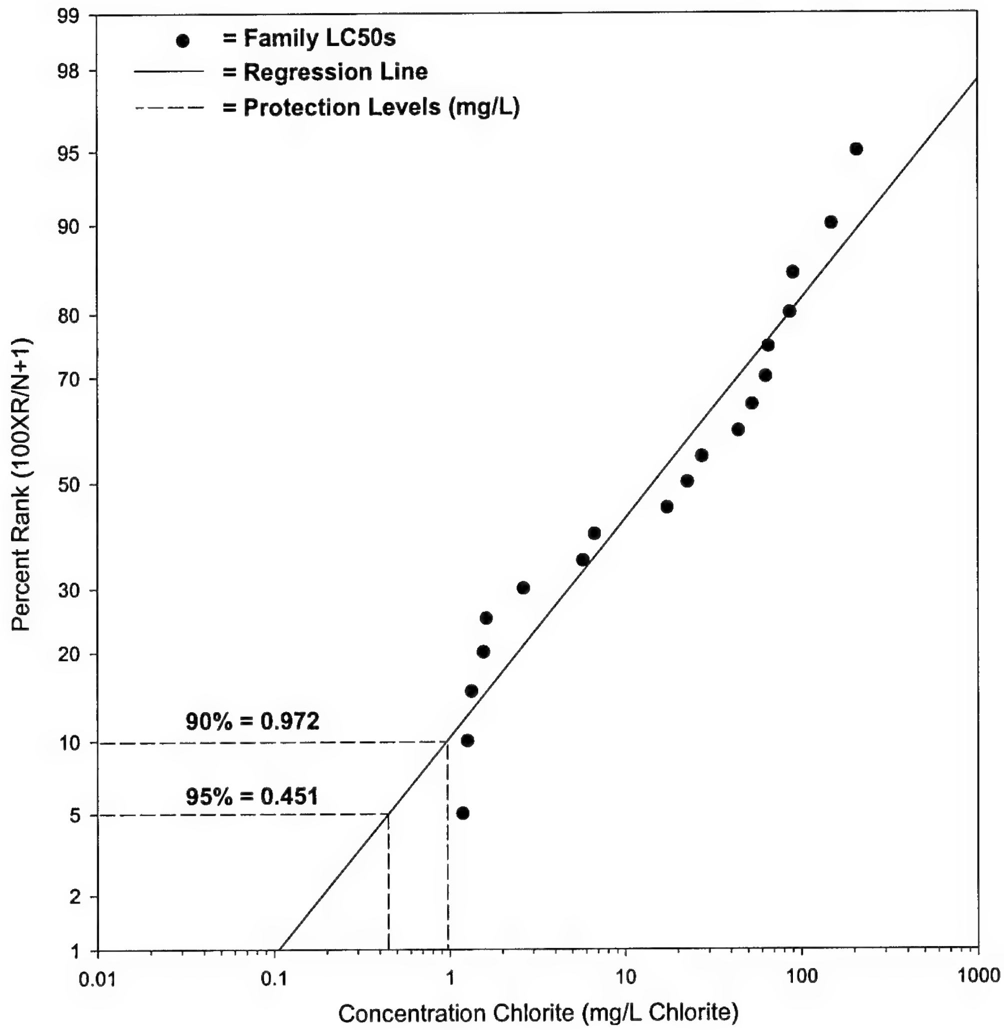

Figure 2.2 LC50 values as family percent rank for all acute toxicity tests less the Daphnidae

for the 20 families less the Daphnidae are 3.3 and 2.1 times greater, respectively, than the protection levels for the 20-family data base which includes the Daphnidae.

CHAPTER 3
CONCLUSIONS

The results of this study show that the EPA water quality criteria method versus the probabilistic approach for calculating protection levels for acute exposure to chlorite give quite different results. The probabilistic calculation, which utilizes all of the toxicity data, provides a 95% protection level over five times greater than the EPA water quality criteria calculation which uses the four most sensitive species. The probabilistic approach for calculating a 95% protection level provides a better fit to the data. It is apparent that the toxicity of chlorite to Daphnidae compared to all the other families is forcing an unreasonably low CMC.

A comparison of the 95 and 90% protection levels with and without Daphnidae indicate that "safe" levels of chlorite may be substantially higher than the proposed acute water quality criterion of 0.135 mg/L as chlorite. A probabilistic ecological risk assessment, which would take into account such things as chlorite usage patterns, exposure concentrations in the receiving stream, relative insensitivities of other larval fish food sources compared to the Daphnidae, etc., should be considered to complete the evaluation of chlorite discharged to surface waters.

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